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## A Metal-Free Heterogeneous Photocatalyst for the Selective Oxidative Cleavage of C=C Bonds in Aryl olefins via Harvesting Direct Solar Energy

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Selective cleavage of C=C bonds is highly important for the synthesis of carbonyl containing fine chemicals and pharmaceuticals. Novel methodologies such as ozonolysis reactions, Lemieux–Johnson oxidation reaction etc. already exist. Parallel to these, catalytic methods using homogeneous catalysts also have been discovered. However, on the verge of recyclability, heterogeneous catalysts are in the forefront and couple of transition metal-based heterogeneous catalysts already exist in the market. However, pharmaceutical industries prefer to use metal-free catalysts (especially transition metal-free) to avoid further leaching in the final products. This is for sure a big challenge to an organic chemist and to the pharmaceutical industries! To make it feasible, a mild and an efficient protocol has been developed using polymeric carbon nitrides (PCN) as the metal-free heterogeneous photocatalyst to convert various olefins into the corresponding carbonyls. Later, this catalyst has been applied in the g-scale synthesis of pharmaceutical drug using direct solar energy. The detailed mechanistic studies revealed the actual role of oxygen, catalyst, and the light source.

#### Figure 1 Methodologies for the oxidative cleavage of olefins.

## Introduction

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Oxidative cleavage of olefins is highly attractive since it generates high-valued oxygen-containing functional groups from the cheap and widely available starting materials (olefins).<sup>1-4</sup> However, the most popular protocols for the C=C bond cleavages are still the old-fashioned ozonolysis reaction and Lemieux–Johnson oxidation reaction, which require either an ozone generator or involve toxic and expensive reagents such as  $O_3$ , osmium tetroxide etc. (Figure 1).<sup>5-6</sup> To replace these, cheaper and safer oxidants such as KMnO<sub>4</sub>, PhIO/HBF<sub>4</sub> etc. have been developed. However, generating over stoichiometric amounts of by-products is pushing them far away from the installation of atom economy in organic synthesis.<sup>7-9</sup>

Compared to the over-stoichiometric oxidants, molecular oxygen can be considered as a clean, cheap oxidant and will be ideal for the oxidative cleavage of olefins.<sup>10-14</sup> For example, Xiao and co-workers developed an excellent method for the selective cleavage using iron catalyst and bisimidazoline ligand under O<sub>2</sub> atmosphere.<sup>15</sup> Later, Feng group have developed a commercially available iron catalyst for this reaction.<sup>16</sup> A binuclear copper complex catalysed system was also described by the Group of Wang which generated the carbonyl

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compounds from terminal alkenes.<sup>17</sup> The first photocatalytic system was reported by the group of Inoue using dimethoxybenzenes as a

sensitizer.<sup>18</sup> Fukuzumi et al. further developed this reaction

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using 10-methylacridinium ion.<sup>19</sup> Furthermore, various developed an excellent cleavage protocol using homogeneous photocatalysts (electron-rich aromatic disulfide, Eosin Y) and catalytic amount of iodine were displayed, respectively.<sup>20</sup> Not only by photocatalysis, Chiba and co-workers developed an excellent electrochemical pathway but it required expensive platinum electrodes to achieve the target conversion.<sup>21</sup>

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Compared to the homogeneous catalysts, a selective heterogeneous catalyst is in high demand due to their post-reaction stability and recyclability.<sup>22</sup> Recently, Cho *et al.* reported a heterogeneous method using BiVO<sub>4</sub> as a photocatalyst.<sup>23</sup> In fact, iron-based heterogeneous catalysts have been also developed, however, they required high O<sub>2</sub> pressure, exhibited limited substrates scope and above all, lack of selectivity in the product distribution.<sup>24-25</sup> So far, only heavy metal based catalytic systems have been discovered. However, pharmaceutical industries prefer to avoid heavy metal based systems to avoid leaching in the final products which could be detrimental for the final use.

We were particularly interested for a metal-free heterogeneous photocatalyst which is currently an interesting avenue in organic synthesis.<sup>26-28</sup> For this purpose, we focused on the polymeric carbon nitrides (PCN) which is easy to synthesize and even commercially available. This catalyst has also exhibited wide applications ranging from water splitting to CO<sub>2</sub> reductions and others.<sup>29-34</sup> Advantageously, PCN have band gap of 2.7 eV (enough to harvest solar energy), where valence band (VB) resides at +1.6 V and conduction band (CB) at -1.10 V.<sup>35</sup> This high CB should be sufficient to generate reactive oxygen species from oxygen (superoxide radical anion  $(O_2/O_2^{\bullet-})$  has the reduction potential of -0.56 V vs SCE) and high positive VB position can be utilized for the oxidation of aryl olefins.<sup>36-38</sup> Additionally, development of solar energy mediated organic transformation is also attractive for the augmentation of sustainable approach in the organic synthesis.<sup>39-40</sup> Indeed, sunlight is renewable and available throughout the entire world. The average intensity of the total solar irradiance is about 1366.1 W m<sup>-2</sup> which provides roughly 4.3x1020 J energy only in 1 h.<sup>41</sup> Therefore, if it is harvested properly and is utilized in the organic synthesis, can solve many of the sustainable issues.<sup>42-43</sup> Owing to the different absorption of organic molecules and also non-uniform irradiation of sunlight, it can be challenging to adopt into the organic synthesis.<sup>39-40</sup> However, if solar energy mediated organic synthesis can be applied via storage of solar energy, it can solve many of the energy intensive synthetic procedures.<sup>42-43</sup> Based on all the above information, herein we report an efficient, metal-free and recyclable heterogeneous photocatalyst which harvested solar energy to cleave the C=C bonds.44

#### **Results and discussion**

At the outset of our reaction, 4-fluoro- $\alpha$ -methylstyrene (1a) was chosen as a model substrate to optimize the reaction conditions (Table 1). At first, different amount of PCN were applied using acetonitrile as the solvent under the irradiation of 12 W blue LED for 24 h. Gratifyingly, 43% of 4-fluoroacetophenone (1b) was achieved using 8 mg of PCN (entries 1–4). However, the increasing amount of catalyst did not improve the yield of the reaction. Furthermore, different additives (10 mol%) such as *N*-hydroxysuccinimide (NHS),

ascorbic acid (AA) and 3-mercaptopropionic acid, (MPA), were investigated (entries 5–7). Among them; <sup>1</sup>addition <sup>C</sup>60<sup>1</sup>NHS increased the formation of the desired product to 61%. Finally, addition of 20 mol% of NHS, increased the yield to 80% of **1b**. However, further loading of NHS did not perform any further improvement (entries 8–9). Trace amount of product formed without the catalyst (entries **10**). Furthermore, investigation of different solvents also did not improve the reaction yield since acetonitrile has higher oxygen solubility than others (entries **11–13**).<sup>45</sup>

**Table 1** Optimization of the C=C bond cleavage using a heterogeneous photocatalyst.<sup>a-e</sup>



Entry	Cat. Amount	additive	Solvent	Yield [%]
1	3 mg	No	CH <sub>3</sub> CN	18
2	5 mg	No	CH₃CN	31
3	8 mg	No	$CH_3CN$	40
4	12 mg	No	$CH_3CN$	43
5	8 mg	AA	CH₃CN	0
6	8 mg	MPA	CH <sub>3</sub> CN	6
7	8 mg	NHS <sup>c</sup>	CH₃CN	61
8	8 mg	NHS <sup>d</sup>	CH₃CN	80
9	0 mg	NHS	CH₃CN	5
10	8 mg	NHS <sup>e</sup>	CH₃CN	79
11	8 mg	NHS <sup>d</sup>	DMSO	46
12	8 mg	NHS <sup>d</sup>	DMF	30
13	8 mg	NHS <sup>d</sup>	DMA	48

[a] General reaction conditions:  $O_2$  balloon, 12 W blue LED, 0.25 mmol of 1a, PCN, 1 mL of acetonitrile, additive, room temperature, 24 h. [b] Yields were determined by GC calibration using dodecane as internal standard. [c] *N*-hydroxysuccinimide (10 mol%). [d] *N*-hydroxysuccinimide (20 mol%). [e] *N*-hydroxysuccinimide (30 mol%).

With these optimized reaction conditions in hand, the scope of the photocatalytic system to other a-substituted styrenes was extended (Scheme 1; entries 2b–17b). To our delight, other substituted  $\alpha$ -methylstyrenes such as 4-chloro- $\alpha$ -methylstyrene, 2-methoxy-a-methylstyrene and 4-methyl- $\alpha$ -methylstyrene generated the corresponding carbonyl compounds in excellent yields (Scheme 1; entries 2b–6b). Furthermore, 1,1'-diphenylethylenes, substituted 1,1'-

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diphenylethylenes also worked excellently to afford the corresponding benzophenone derivatives (Scheme 1; entries 7b-9b). Meanwhile, other a-substituted styrene derivatives such as  $\alpha$ -*n*-propylstyrene,  $\alpha$ -*n*-butylstyrene and  $\alpha$ -*iso*butylstyrene etc. exhibited moderate to high yields of the corresponding ketones (Scheme 1; entries 10b-14b). Further investigations towards the hetero-aromatic ring substituted styrenes were also carried out. Indeed, these substrates reacted smoothly to form the 4-benzoylpyridine, 2-benzoylpyridine and 2-(Prop-1-en-2-yl)thiophene with excellent isolated yields (Scheme 1; entries 15b-17b). It should be also noted that in none of the cases corresponding epoxides, diols or further allylic and oxygenated products were observed thereby demonstrated high selectivity of the photocatalyst.

Scheme 1 Scope of the C=C bond cleavage of a-substituted styrenes.  $^{\rm a-b}$ 



[a]  $O_2$  balloon, 12 W blue LED, 0.25 mmol of starting material, 8 mg of PCN, 1 mL of acetonitrile, 20 mol% of *N*-hydroxysuccinimide, room temperature. [b] isolated yields.

Next, we became interested to apply the photocatalytic system to mono-substituted olefins since they could afford high-valued aldehydes. For example, veratraldehyde **(21b)** is a key intermediate for the synthesis of many of the pharmaceuticals such as verazide, amiquinsin, hoqquizil, and so on.<sup>46</sup> To our delight, this heterogeneous photocatalyst exhibited medium to good reactivity towards the mono-substituted styrenes such as

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Scheme 2 Scope of the C=C bond cleavage of terminal styrenes.<sup>a-b</sup>



[a]  $O_2$  balloon, 12 W blue LED, 0.25 mmol of starting material, 8 mg of PCN, 1 mL of acetonitrile, 20 mol% of *N*-hydroxysuccinimide, room temperature. [b] isolated yields.

Scheme 3 Scope of the C=C bond cleavage of  $\beta\text{-substituted styrenes}$  and  $\alpha\text{-bromo styrenes.}^{a\text{-}b}$ 



[a] Reaction conditions: air, 12 W blue LED, 0.25 mmol of starting material, 8 mg of PCN, 1 mL of acetonitrile. [b] isolated yields.

Inspired by the excellent reactivity, we were interested to expand the substrates scope only using the heterogeneous photocatalyst (Scheme 3; entries 22b–26b). Besides the model substrate (1a) (see Table 1, entry 3), anethole, trans- $\beta$ -methylstyrene, etc. also exhibited moderate activities even under air (22b–26b). To our surprise,  $\alpha$ -bromostyrene derivatives underwent the migration of the bromide to the  $\beta$ -carbon and formed the phenacyl bromide derivatives (27b-29b).<sup>15</sup> It should be noted that some of the complex molecules such as triacetylresveratrol (Scheme 4, 30a),<sup>47</sup> trans-

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chlorprothixene (**31a**),<sup>48</sup> are highly challenging molecules to cleave under the normal circumstances. Notably, with this robust photocatalyst, selective cleavage of these complex

molecules generated the corresponding oxygenated products in high yields. DOI: 10.1039/D0GC01187H

Scheme 4 Scope of the C=C bond cleavage of complex molecules.<sup>a-b</sup>



[a] O<sub>2</sub> balloon, 12 W blue LED, 0.25 mmol of starting materials, 8 mg of PCN, 1 mL of acetonitrile, 20 mol% of *N*-hydroxysuccinimide, room temperature. [b] isolated yields.

### Scheme 5 Direct solar energy mediated C=C bond cleavage in g-scale.



As we mentioned in the introduction, natural sunlight is an inexpensive and widely available energy source. Therefore, we sought to harvest direct solar energy for the selective cleavage of C=C bonds. Not only the small molecule (**5a**) was cleaved into the corresponding ketone, but the complex molecule such as **32a**, was also cleaved selectively under the sunlight. These reactions were easily scaled up to *g*-scale. Additionally, fenofibrate, a pharmaceutical drug used for the treatment of abnormal lipid levels, was synthesized in *g*-scale from the corresponding olefin (**Scheme 5**; **entry 35b**).<sup>49</sup>

To ensure the stability and reusability of the photocatalyst, PCN was recycled multiple times under the optimized reaction conditions. In fact, catalyst was recycled 5 times and can be reused further (**Figure S5**). To further investigate the stability of PCN catalyst, elemental analysis (**Table S1**), X-ray powder diffraction (XRD) fourier-transform

infrared spectroscopy (FTIR), UV/Vis, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) were measured and compared the difference between the freshly prepared catalyst and the recycled catalyst. Analysis of the catalyst before and after a reaction using XRD showed the same characteristic peaks at 27.3° and 13.2° which is also matched with literature report (Figure S6).50-51 From the UV-Vis and FTIR, no difference in the absorbance was observed. TEM and SEM revealed the morphology of the PCN particles before and after the recycling. They formed rounded plates with an average diameter of (30±10) nm and a thickness of the order of a few angstrom. Due to the agglomeration, bigger particles were composed by the stacks of the plates. No significant changes in the morphology was observed with TEM (Figure 2 [d-e]) and SEM (Figure S6) after recovering the catalyst. To get more insight into the crystal structure, selected area electron diffraction measurements were carried out. The diffuse rings did not exhibit any sign of crystallinity. A more detailed analysis of the intensity profile did not provide any evidence of a change during catalysis. In addition, the HRTEM images demonstrated clearly the amorphous nature of the catalyst.

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**Figure 2** Analysis of new and recovered PCN by FTIR [a], UV/Vis [b], intensity profile of the selected area electron diffraction pattern (SAED) [c], brightfield TEM [d-e] as well as HRTEM with SAED as an inset [f-g].

Inspired by the generality of the substrates scope, we sought to gather mechanistic information about the role of the light, oxygen, catalyst and additive in our reactions. According to the control experiments, no product was observed in the absence of light, photocatalyst and oxygen. Only trace amount of the product was observed in the presence of the additive which clearly demonstrated the necessity of the photocatalyst and oxygen in the reaction (**Table S2**). Further, on/off light experiments were also performed to prove that the yield of the product was completely suppressed in the absence of light (**Figure 3**).

Furthermore, the effect of different quenchers was investigated to figure out the reactive oxygen species and possible intermediates in our reactions (**Table 2**).<sup>52</sup> When 2,6-di-tert-butyl-4-methylphenol (BHT) or 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) were added, the yield was dramatically decreased which proved that the reaction was undergoing a radical pathway. Further addition of benzoquinone in the reaction displayed the presence of superoxide radical anion. Furthermore, addition of CuCl<sub>2</sub> and catalase to the reaction mixture showed lower yields which proved that there could be involvement of single electron processes and the presence of peroxide species in this reaction.

**Figure 3** On/off light experiments of 4-(1-Propenyl)-1,2dimethoxybenzene.<sup>a-b</sup>



[a]  $O_2$  balloon, 12 W blue LED, 0.25 mmol of starting material, 8 mg of PCN, 1 mL of acetonitrile, 20 mol% of *N*-hydroxysuccinimide, room temperature. [b] Yields were determined by NMR using iodoform as an internal standard.

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Table 2 Quenching experiments for the C=C bond cleavage.<sup>a-b</sup>

F CH2CN (8 mg) NH5 (20 m0!%) CH3CN (1 mL) quencher blue LED, 24 h							
Quenchers	Equivalents	Yield [%]	Conclusions				
BHT	0.5	0	radical				
TEMPO	0.5	0	radical				
tert-butanol	1.0	42	hydroxide radical				
CuCl <sub>2</sub>	1.0	46	single electron				
Catalase	100 mg	9	peroxide radical				
Benzoquinone	1.0	2	superoxide radical				
Soduim azide	2.0	43	singlet oxygen				

[a]  $O_2$  balloon, 12 W blue LED, 0.25 mmol of starting material, 8 mg of PCN, 1 mL of acetonitrile, 20 mol% of *N*-hydroxysuccinimide, room temperature, different quenchers. [b] Yields were determined by GC analysis using *n*-dodecane as an internal standard.

To get further information about the reaction mechanism, Stern-Volmer quenching experiments were carried out (**Figure 4**) which is clear that the excited state of the photocatalyst was quenched by the olefin and not by the oxygen or additive.<sup>52</sup> To show the actual source of oxygen in the product, reaction was investigated under <sup>18</sup>O-labelled oxygen atmosphere. To our delight, only <sup>18</sup>Olabelled product (**37**) was observed and isolated from the reaction. Interestingly, we also detected the <sup>18</sup>O-labelled intermediate (**36**) in this reaction, and in this case both of the oxygen atoms in dioxetane came from the oxygen atmosphere (**Figure 5**).

Figure 4 Stern-Volmer plot for the different concentrations of olefins,  $O_2$  and additive.



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Combing all the mechanistic information, mechanism of this reaction was proposed (Figure 5). At first, visible-light irradiation created charge separation in PCN, produced oxidative valence band and reductive conduction-band.<sup>40</sup> Then the conduction-band electron reduced the oxygen to produce superoxide radicals. The valence band hole oxidized 1a to the corresponding radical cation 1c. This radical cation 1c combined with the superoxide radical anion and 1f was formed via [2+2] cycloaddition. However, there was another pathway (pathway B) which involved the additive Nhydroxysuccinimide (NHS). Firstly, 1h was generated through NHS (1g) via hydrogen atom transfer (HAT).53 Meanwhile, the hydrosuperoxide anion was generated. Afterwards, 1h attacked 1a to form the cation 1d which further reacted with hydrosuperoxide anion to afford 1e which later formed the intermediate 1f by releasing NHS. At last, the cleavage of dioxetane 1f generated the final product (1b).

Figure 5 (a) Oxygenation of of 4-fluoro- $\alpha$ -methylstyrene in the presence of <sup>18</sup>O<sub>2</sub>; (b) Plausible mechanism of this reaction.



## Conclusions

In summary, polymeric carbon nitrides (PCN) as a photocatalyst has been developed for the selective cleavage of C=C bonds in aryl olefins. This method was selective, scalable under the presence of sunlight and the photocatalyst was easily recyclable. Excellent substrate scope with high selectivity is the main advantage of this recyclable catalyst. In addition to these, we have been able to perform the late-stage C=C bond cleavage in aryl olefins and degradation of complex molecules to achieve highly valuable products and pharmaceuticals. The stability of PCN has been well investigated by different spectroscopic analyses. We believe this protocol can be applied and extended for the cleavage of olefins in bulk chemistry, for the syntheses of pharmaceuticals and natural product.

## **Conflicts of interest**

There are no conflicts to declare.

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TOC:

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Solar energy mediated

Metal-free catalystRecyclable catalyst

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Wide substrates scope

Synthesis of pharmaceuticals

Cleavage of complex molecules